Heavy metals in feed - Current regulation, risk assessment, methods of analysis, examples and future trends

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Publication date:
2011

Document Version
Publisher's PDF, also known as Version of record

Heavy metals in feed

Current regulation, risk assessments, methods of analysis, examples and future trends

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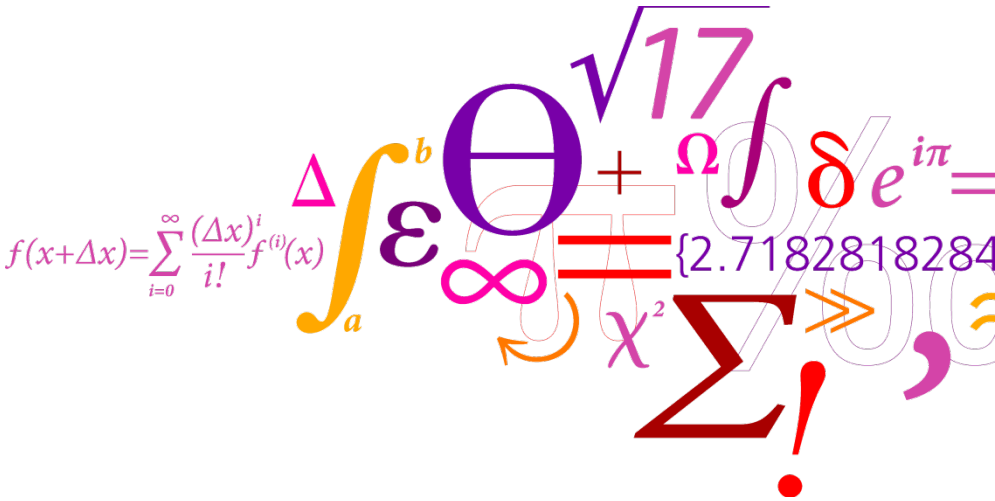

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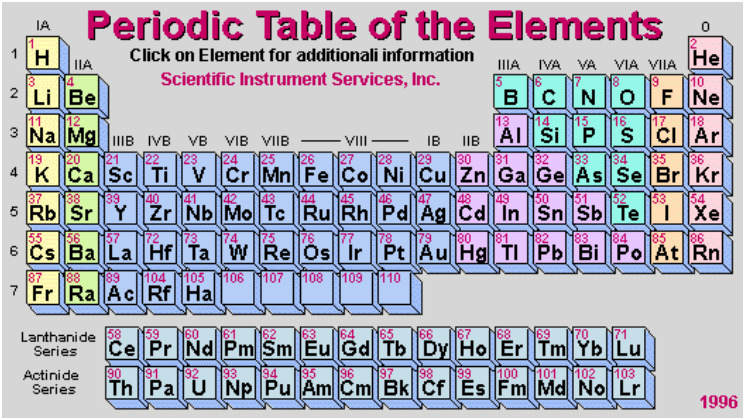
Agenda

Selected topics in the presentation

- Heavy metals of highest priority
- Risk assessment and regulation on heavy metals in feed
- Methods of analysis for metals in feed
- Speciation of metals – for improved risk assessment



Heavy metals – definition??

IUPAC: HEAVY METALS – A MEANINGLESS TERM?
(Duffus, Pure and Appl Chem 2002)

Many different definition can be found in the literature –
but no official definition exists.

The Heavy metals are a range of elements with high density and are in metallic form at room temperature
(High density- > 3,5 kg/m³ - > 7,8 kg/m³ (=Fe)) – atomic number > Na (23)

Some are very toxic – lead, cadmium, mercury
Others are essential – chromium, cobolt, cupper, iron, manganese, zinc

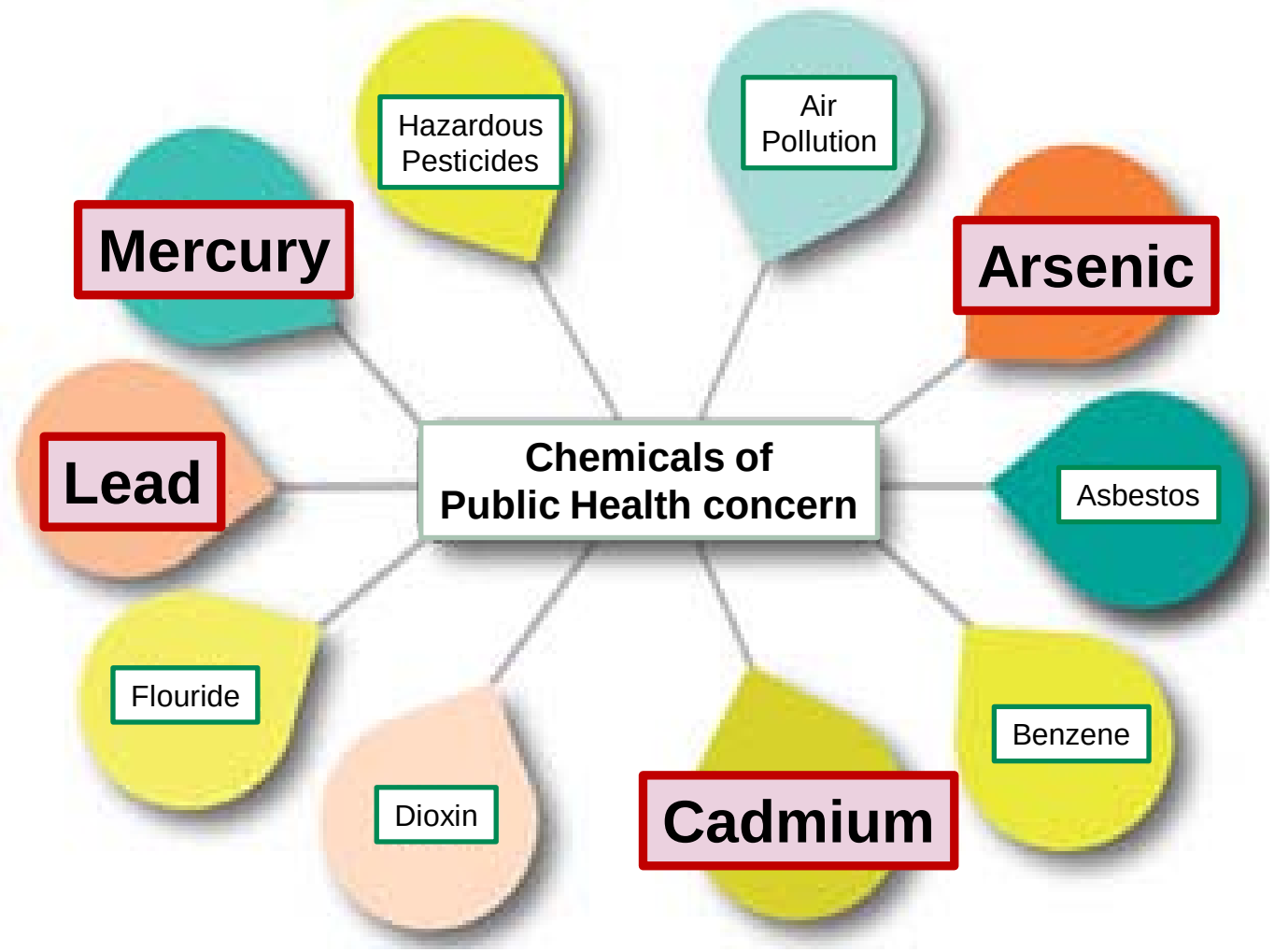
In the public perception:
heavy metals = elements with toxic properties

TOXIC METALS

The International Programme on Chemical Safety (IPCS)

WHO ILO UNEP

DTU



4 metals on the WHO IPCS list of top-10 priority chemicals of public concern

http://www.who.int/ipcs/

Toxicity of heavy metals

- Toxicity is mainly due to binding to sulphur-containing enzymes => inhibition of functions
- Affect cell membrans => effect on transport-mecanisms
- Bioaccumulation in the body
- Biomagnification through the food chain

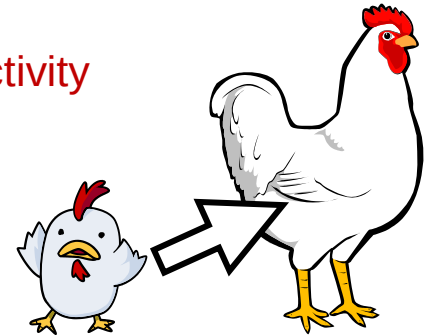
•	Cadmium	-toxicity on the kidneys
		-osteoporosis
		-itai-itai disease (Cd poisoning)
•	Lead	-effects on CNS
		-cognitive deficits on children
•	Mercury	-minamata disease (MeHg poisoning)
		-cognitive effects
•	Arsenic	-blackfoot disease and other skin diseases
		-cancer (lung, skin and bladder)

Sources of heavy metals

- **Natural sources**
  - Volcanic activity
  - Rocks and minerals
  - Atmospheric deposition

- **Anthropogenic sources**
  - Agricultural activities (fertilisers, manure, pesticides)
  - Mining activities
  - Industrial disposals

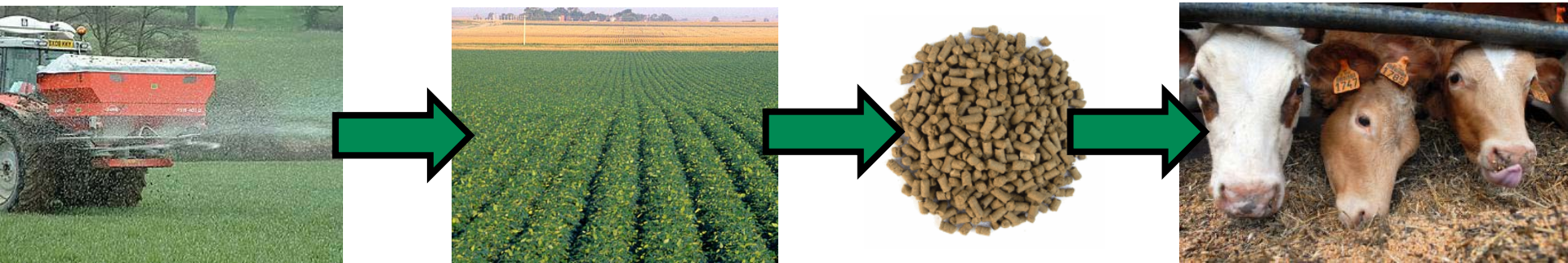
- Cadmium
  - -high levels in soils
  - -forage crops (root>leaves>stem>fruits/grains)
  - -application of sewage sludge and P fertilisers
  - -atmospheric deposition-> crops
- Lead
  - -atmospheric deposition-> crops
  - -mining/industrial activity
  - -sewage sludge -> soil - crops
- Mercury
  - -fishmeal
  - -atmospheric deposition
- Arsenic
  - -weathering of minerals/volcanic activity
  - -pesticides ($PbAsO_4$, CCA)
  - -growth promotors



Feed -> food – some examples

- **Cd**: P fertilisers -> soil -> crops -> feed -> domestic animals (high in offal)
- **Hg**: Marine fishmeal -> fish feed -> aquaculture products

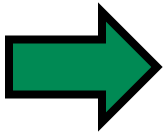
  (alternative sources: protein of vegetable origin)
- **Pb, Cd**: Mineral mixes (as impurities) -> feed -> domestic animals
- **As**: Roxarsone (As growth promoter) -> feed -> poultry
- **??**: Industrial byproducts -> feed



EFSA risk assessments of feed

Cadmium	Opinion of the Scientific Panel on Contaminants in the Food Chain on a request from the Commission related to **cadmium** as undesirable substance in animal feed (2004)
Lead	Opinion of the Scientific Panel on Contaminants in the Food Chain on a request from the Commission related to **lead** as undesirable substance in animal feed (2004)
Arsenic	Opinion of the Scientific Panel on Contaminants in the food chain on a request from the Commission related to **arsenic** as undesirable substance in animal feed (2005)
Mercury	**Mercury** as undesirable substance in animal feed Scientific opinion of the Panel on Contaminants in the Food Chain (2008)
27 elements	Selected trace and ultratrace elements: Biological role, content in feed and requirements in animal nutrition – Elements for risk assessment (2010)

EFSA opinions on exposure from food



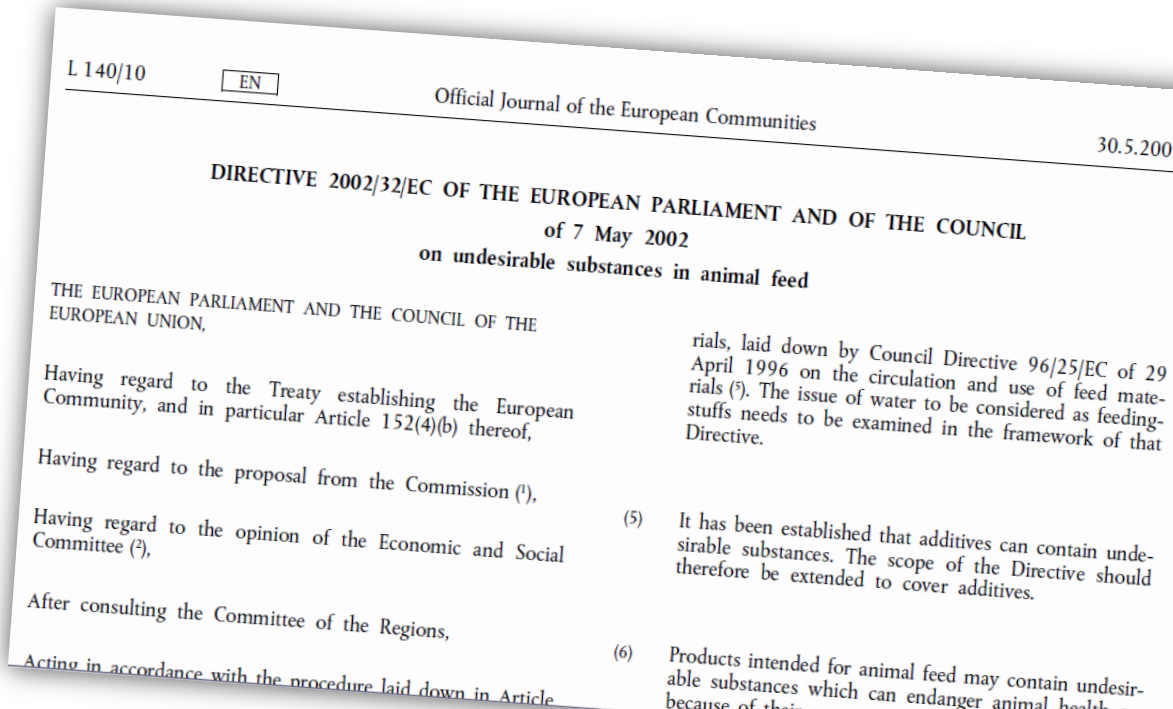
Cadmium (2009)
- PTWI from 7 -> 2,5 µg/kg bw/week.
- Intake close to PTWI for many populations
- Exposure should be reduced

Lead (2010)
- PTWI at 25µg/kg bw/week not appropiate
- Low margin of exposure (MoE)
- Special focus on children and pregnant women

Arsenic (2009)
- PTWI from 15 µg/kg bw/week -> BMDL 0,3-8 µg/kg bw/day
- Intake within BMDL for average and high consumers
- Exposure should be reduced

Legislation

- The maximum levels are regulated according to EU directive 2002/32/EC on undesirable substances in animal feed
- Be aware of later amendments (e.g. 2010/6/EC - > changes for Hg)
- Maximum levels for arsenic, cadmium, lead and mercury
- Various feed materials and compound feeds are regulated, e.g.:
  - Feedingstuffs produced from fish…
  - Calcium carbonate
  - Mineral feed
  - Feed for fish



L 140/10 EN Official Journal of the European Communities 30.5.200

DIRECTIVE 2002/32/EC OF THE EUROPEAN PARLIAMENT AND OF THE COUNCIL
of 7 May 2002
on undesirable substances in animal feed

THE EUROPEAN PARLIAMENT AND THE COUNCIL OF THE EUROPEAN UNION,

Having regard to the Treaty establishing the European Community, and in particular Article 152(4)(b) thereof,

Having regard to the proposal from the Commission (1),

Having regard to the opinion of the Economic and Social Committee (2),

After consulting the Committee of the Regions,

Acting in accordance with the procedure laid down in Article

rials, laid down by Council Directive 96/25/EC of 29 April 1996 on the circulation and use of feed materials (5). The issue of water to be considered as feedingstuffs needs to be examined in the framework of that Directive.

(5) It has been established that additives can contain undesirable substances. The scope of the Directive should therefore be extended to cover additives.

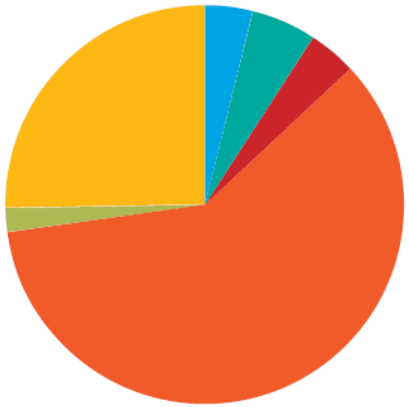
(6) Products intended for animal feed may contain undesirable substances which can endanger animal

Legislation – example - cadmium

Products intended for animal feed	ML (mg/kg)
Feed materials of vegetable origin	1
Feed materials of animal origin	2
Feed materials of mineral origin except	2
– phosphates	10
Additives belonging to the functional group of compounds of trace elements except	10
– copper oxide, manganous oxide, zinc oxide and manganous sulphate monohydrate	30
Premixtures	15
Mineral feedingstuffs **– containing < 7 % phosphorus** **– containing ≥ 7 % phosphorus**	 5 0,75 per 1% P (max 7,5)
Complete feedingstuffs for cattle, sheep and goats and feedingstuffs for fish except	1
– complete feedingstuffs for pets **– complete feedingstuffs for calves, lambs and kids and other complete feedingstuffs**	2 0,5

Rapid Alert system (RASFF) – Annual report 2009

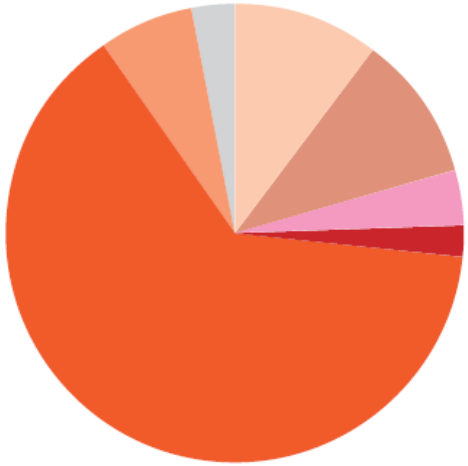
RASFF FEED NOTIFICATIONS IN 2009: PRODUCTS AND HAZARDS



- pet food
- feed premixtures
- feed materials
- feed additives
- compound feeds
- animal by-products

	arsenic	cadmium	lead	mercury	tin
bivalve molluscs		1			
cephalopods		15			
cereals and bakery products		2			
cocoa, coffee and tea			1		
Compound feeds				1	
crustaceans		37			
dietetic foods	8		8	2	
Feed additives	1	2	1		
Feed materials	2	2	1		
fish		6		92	
fruit and vegetables	4	4	6		5
meat			1		

FEED MATERIALS



- other
- mycotoxins
- microbiological contamination
- industrial contaminants
- heavy metals
- GMO
- foreign bodies

RASFF, Report 2009

EU-RL – Heavy metals in feed and food

Coordinated by JRC-IRMM in Geel, Belgium

- *facilitate the implementation of Directive 2002/22/EC*
- *organise interlaboratory comparisons for NRLs*
- *support and advice to the European authorities and the NRLs on scientific matters*
- *training of NRL personnel (annual workshop)*

www.irmm.jrc.ec.europa.eu/EURLs/EURL_heavy_metals

Standardised methods of analysis

European Committee for Standardization
Comité Européen de Normalisation
Europäisches Komitee für Normung

- TC327 – Animal feedingstuffs – methods of sampling and analysis
- WG4 – Heavy metals, trace elements and minerals
  - *Secretariat by NEN (Dutch Standardisation Organisation)*
  - *Convenor Mr. Jürgen Danier from TÜM*
  - *WG expert members from various EU countries*

- Method performance tested in full collaborative trials
  - *According to ISO5725-2*
  - *Min 8 valid sets of results from different labs*
- Method procedure and results discussed in WG4
- Formally approved by EU MS before being issued as ENs

Standardised methods of analysis

European Committee for Standardization
Comité Européen de Normalisation
Europäisches Komitee für Normung

- **EN15550:2007** - Animal feeding stuffs - Determination of **cadmium** and **lead** by graphite furnace atomic absorption spectrometry (GF-AAS) after pressure digestion
- **EN15510:2007** - Animal feeding stuffs - Determination of calcium, sodium, phosphorus, magnesium, potassium, iron, zinc, copper, manganese, cobalt, molybdenum, **arsenic**, **lead** and **cadmium** by ICP-AES
- **prEN16206** - Animal feeding stuffs - Determination of **arsenic** by hydride generation atomic absorption spectrometry (HGAAS) after microwave pressure digestion (digestion with 65 % nitric acid and 30 % hydrogen peroxide)
- **prEN16277** - Animal feeding stuffs - Determination of **mercury** by cold-vapour atomic absorption spectrometry (CVAAS) after microwave pressure digestion (extraction with 65 % nitric acid and 30 % hydrogen peroxide)
- **prEN16278** - Animal feeding stuffs - Determination of **inorganic arsenic** in feed of marine origin by SPE-HG-AAS

Methods of analysis

- Standardised methods of analysis – metals in feed - overview

European Committee for Standardization
Comité Européen de Normalisation
Europäisches Komitee für Normung

CEN no	Element(s)	Pretreatment	Detection
EN15510:2007	As, Pb, Cd and others	Pressure digestion	ICP-AES
EN15550:2007	Cd, Pb	Pressure digestion	GF-AAS
prEN16206	As (total)	Pressure digestion	HG-AAS
prEN16277	Hg (total)	Pressure digestion	HG-AAS
prEN16278	As, inorganic	Extraction	SPE-HG-AAS

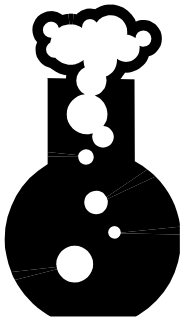
Proposed future standard methods:

- Multielement method (incl Cd, Pb, Hg, As) by ICPMS following pressure digestion
- Inorganic arsenic by HPLC-ICPMS (feed materials and compound feed)
- Determination of iodine in feeding stuffs by ICP-MS
- Criteria approach for methods of analysis

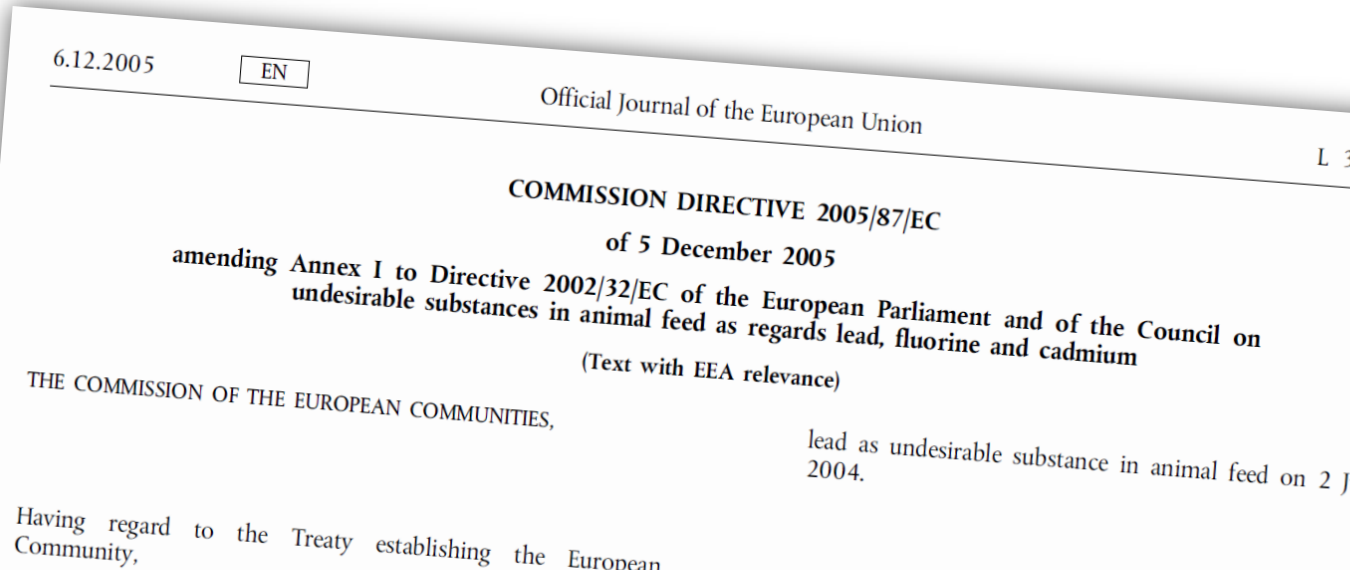
EU Directive 2002/32/EC

- Amendment 2005/87/EC – footnote

- *”Maximum levels refer to an analytical determination of lead and cadmium whereby extraction is performed in nitric acid 5% (W/W) for 30 minutes at boiling temperature. Equivalent extraction procedures can be applied for which it can be demonstrated that the used extraction procedure has an equal extraction efficiency.”*



- Difference between total digestion and extractable content??



6.12.2005 EN Official Journal of the European Union L

COMMISSION DIRECTIVE 2005/87/EC

of 5 December 2005

amending Annex I to Directive 2002/32/EC of the European Parliament and of the Council on undesirable substances in animal feed as regards lead, fluorine and cadmium

(Text with EEA relevance)

THE COMMISSION OF THE EUROPEAN COMMUNITIES,

lead as undesirable substance in animal feed on 2 J
2004.

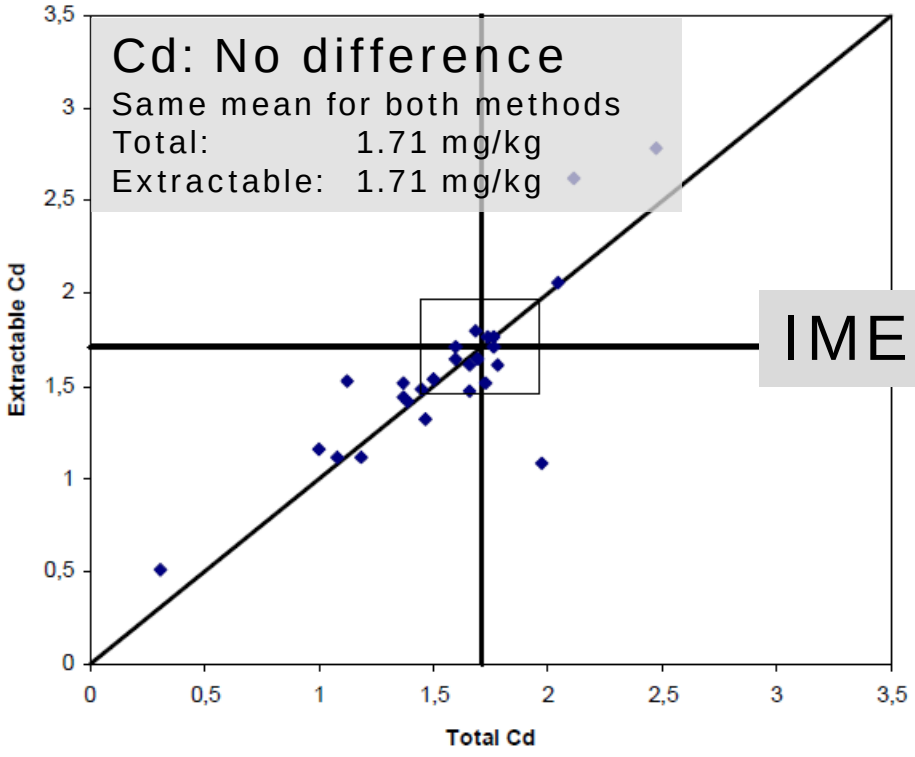
Having regard to the Treaty establishing the European Community,

Difference in results compared to total digestion??

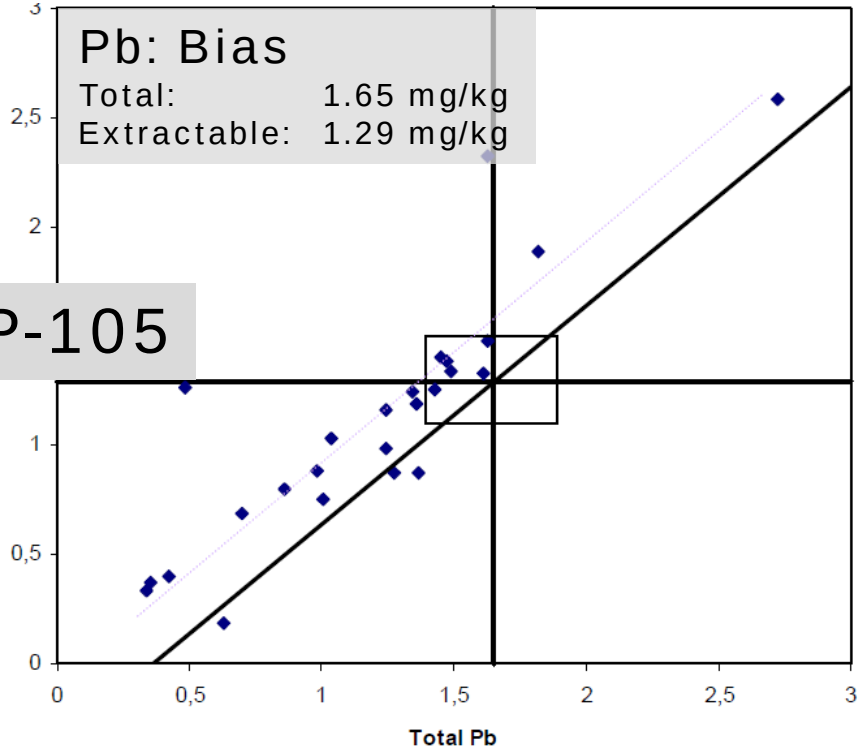
Interlaboratory comparison studies by EURL

- ***IMEP-103 Fish feed***
- *IMEP-105 Mineral feed for piglets*
- ***IMEP-108 Rye grass***
- ***IMEP-111 Mineral feed (phosphate rock)***

In most cases no difference in total and extracted content



IMEP-105



Ref: IMEP-105 report

Animal feedingstuffs

Commission directive 2009/114/EC (amendment)

Undesirable substances	Products intended for animal feed	Maximum content in mg/kg (ppm) relative to a feedingstuff with a moisture content of 12 %
(1)	(2)	(3)
'1. Arsenic (*) (**)	Feed materials with the exception of:	2
	— meal made from grass, from dried lucerne and from dried clover, and dried sugar beet pulp and dried molasses sugar beet pulp,	4
	— palm kernel expeller,	4 (***)
	— phosphates and calcareous marine algae,	10
	— calcium carbonate,	15
	— magnesium oxide,	20
	— feedingstuffs obtained from the processing of fish or other marine animals, including fish,	25 (***)
	— seaweed meal and feed materials derived from seaweed,	40 (***)
	Iron particles used as tracer.	50
	Additives belonging to the functional group of compounds of trace elements except:	30
	— zinc oxide, manganese oxide and copper oxide,	100
	Complete feedingstuffs with the exception of:	2
	— complete feedingstuffs for fish and complete feedingstuffs for fur animals,	10 (***)
	Complementary feedingstuffs with the exception of:	4
	— mineral feedingstuffs,	12

Only max levels for total arsenic

FOOTNOTE

(***) Upon request of the competent authorities, the responsible operator must perform an analysis to demonstrate that the content of **Inorganic arsenic lower than 2 ppm** is of particular importance for the seaweed species *Hizikia fusiforme*.'

Speciation analysis is required !!

Total *vs* inorganic arsenic in fish feed products

Product	N	Mean	Range
Complete feedingstuffs	39	5.8	3.4 - 8.3
Fish meal	10	7.7	3.6 - 18.2
Fish oils	6	11.2	9.1 - 13.5

Total As

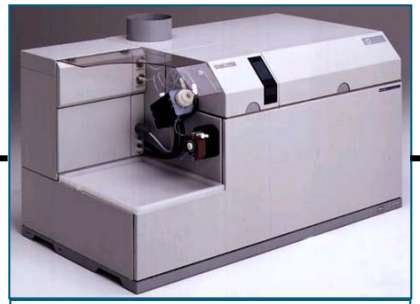
Results in mg kg^{-1}

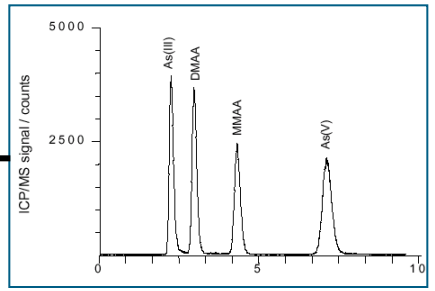
Product	N	Range	% of total As
Complete feedingstuffs	13	0.010 – 0.06	0.18 - 1.20
Fish meal	10	All < 0.007	-

Inorganic As

Sloth et al, Aquaculture Nutr., 2005, 11, 61-66

Methods for speciation analysis of arsenic – Workhorse: HPLC-ICPMS





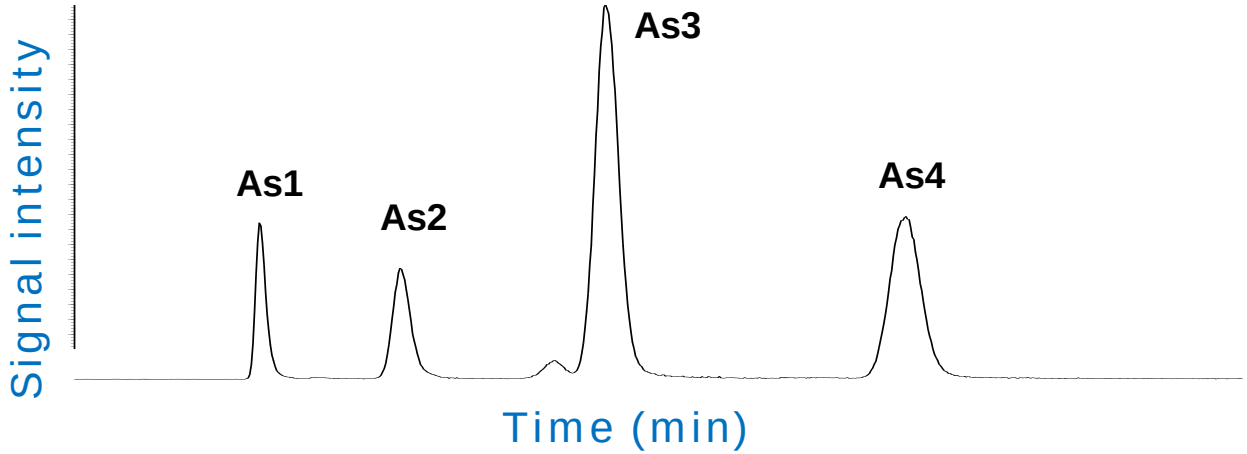
HPLC
Sample introduction

Column
Separation

ICPMS
Element specific detection

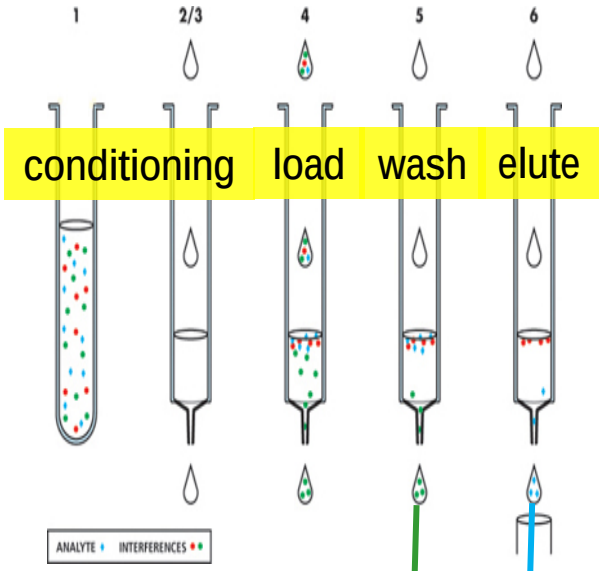
Result
Chromatogram

Output:
Arsenic specific chromatogram

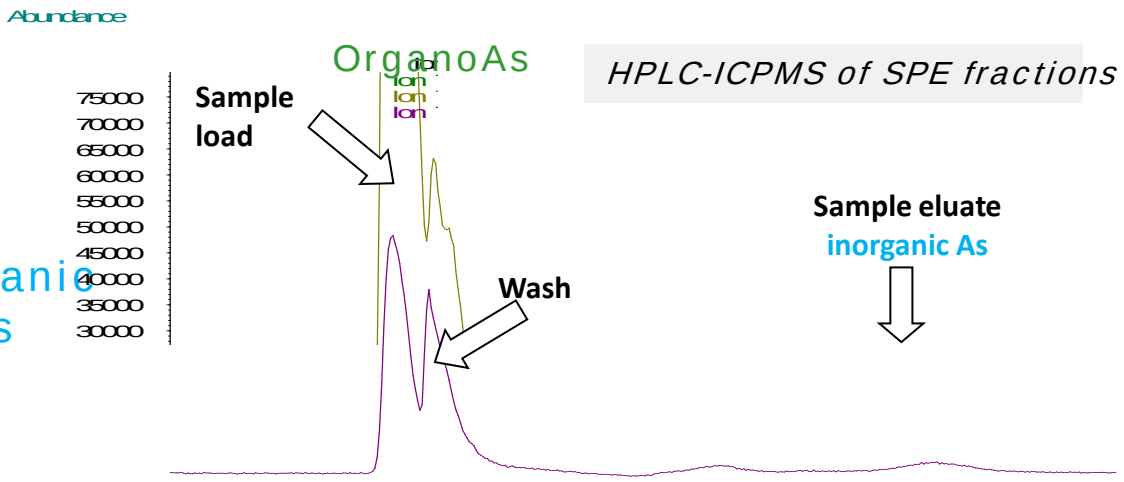


SPE-HG-AAS – a speciation alternative…

μ-wave extraction → Separation by SPE → Detection by HG-AAS



Sequential elution for selective off-line separation of inorg As from organo As species by SPE



HPLC-ICPMS of SPE fractions

Rasmussen & Sloth, in prep

SPE-HG-AAS

In-house validation data

www.conffidence.eu

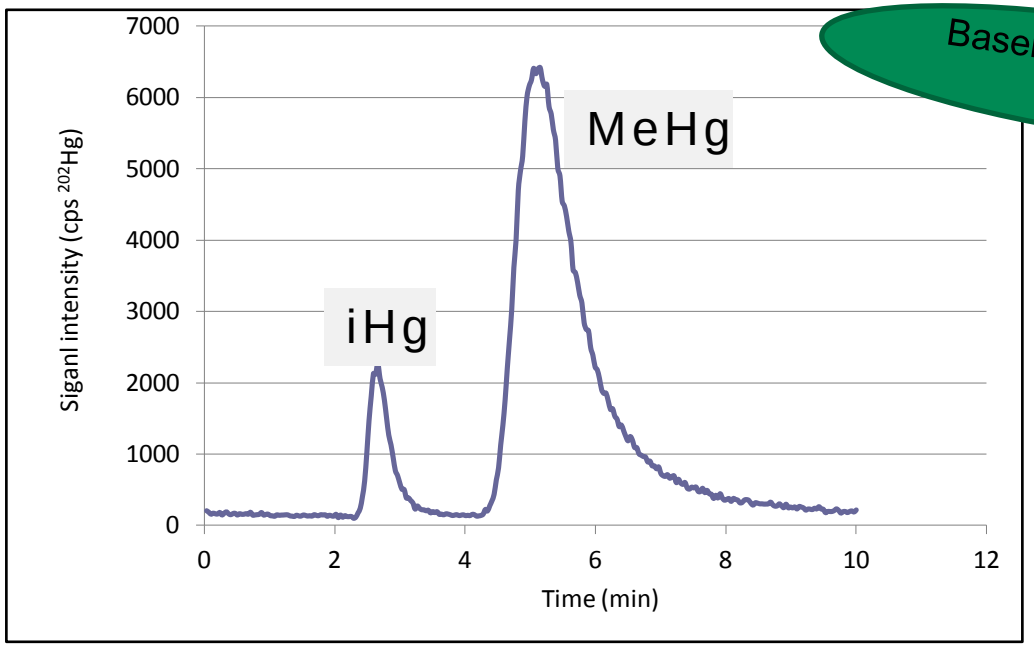
Parameter	Result
Analysis time	2 x 7 h for 24 samples
LoD (mg/kg)	0.08
LoQ (mg/kg)	0.16
Repeatability (%RSD)	3 - 7
Accuracy (%)	90 - 104

Collaborative trial in marine feed material

- 10 labs provided compliant results
- Method working range tested: 0.1 – 2.6 mg Kg^{-1}
- HorRat values <2 in the working range tested
- The method is fit for purpose
- Final publication as EN16278 expected July 2012

Speciation analysis of Mercury by HPLC-ICPMS

www.conffidence.eu



HPLC-ICPMS chromatogram of DORM-3 (Dogfish muscle)

CRM	Certified (mg/kg)	Result (mg/kg)
DORM-2 (dogfish muscle)	4.47 +/- 0.32	4.21
DORM-3 (dogfish muscle)	0.355 +/- 0.056	0.35
TORT-2 (Lobster hepatopancreas)	0.152 +/- 0.013	0.16

Method in-house validated for marine food and feed

Further information

Legislation: www.eur-lex.europa.eu

Risk assessments: www.efsa.europa.eu

RASFF: www.ec.europa.eu/food/food/rapidalert

Funding and acknowledgements

- EU 7th framework project: CONffIDENCE (www.conffidence.eu)
- European standardisation Organisation (CEN)

- Rie R. Rasmussen, Erik H. Larsen, Birgitte K. Herbst

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